

Dynamical coupling between off-plane phonons and in-plane electronic excitations in superconducting YBCO

Daniele Fausti,^{1,2} Fabio Novelli,² Gianluca Giovannetti,³ Adolfo Avella,^{4,5} Federico Cilento,² Luc Patthey,⁶ Milan Radovic,^{6,7} Massimo Capone,³ and Fulvio Parmigiani^{1,2,8}

¹*Department of Physics, Universit degli Studi di Trieste, 34127 Trieste, Italy*

²*Sincrotrone Trieste SCpA, 34127 Basovizza, Italy**

³*CNR-IOM Democritos National Simulation Center and Scuola Internazionale Superiore di Studi Avanzati (SISSA), Via Bonomea 265, 34136 Trieste, Italy*

⁴*Dipartimento di Fisica, E.R. Caianiello - Unità CNISM di Salerno, Università degli Studi di Salerno, I-84084 Fisciano (SA), Italy*

⁵*CNR-SPIN, UoS di Salerno, I-84084 Fisciano (SA), Italy*

⁶*SwissFEL, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*

⁷*Institut de la Matière Complexe, EPF Lausanne, CH-1015 Lausanne, Switzerland*

⁸*International Faculty, University of Cologne, (Germany)*

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The interaction between phonons and high-energy excitations of electronic origin in cuprates and their role on the superconducting phenomenon is still controversial. Here, we use coherent vibrational time-domain spectroscopy together with density functional and dynamical mean-field theory calculations to establish a direct link between the c-axis phonon modes and the in-plane electronic charge excitations in optimally doped YBCO. Our findings clarify the nature of the anomalous high-energy response associated to the formation of the superconducting phase in the cuprates.

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The role played by phonons in cuprates superconductivity is still controversial. While on one hand a purely phononic mechanism can hardly account for the superconducting properties[1, 2], on the other hand strong anomalies are visible in the phonon sub-system upon entering the superconducting phase in most cuprates[3, 4]. Furthermore, non-standard fingerprints of electron-phonon interaction have been observed as a result of the interplay with strong electron-electron correlations[5]. A common feature of the cuprates, confirming the complexity of the riddle posed by these materials, is that the onset of the superconducting phases is accompanied by large changes in the optical properties up to energies of order of few electronvolts[6–9], ten times larger than the typical superconducting gaps (10-100 meV). This is in striking contrast with a BCS scenario in which the variations of the optical properties at the superconducting phase transition are limited to energies of the order of the gap. Such an unusual behavior reveals the strong interconnection between high-energy processes, mainly controlled by electron-electron correlations, and the low-energy excitations relevant in the pairing mechanism of the cuprates[10].

Here, we report on a novel approach, based on time-domain broadband spectroscopy, density functional theory (DFT), and dynamical mean field theory (DMFT)[11], to address the interplay between vibrational modes and the high-energy electronic response in the cuprates. Our measurements and calculations rationalize the different coupling of the barium (Ba) and copper (Cu) c-axis A_{1g} modes to the superconducting phase

and highlight the importance of the coupling between electrons and specific lattice modes in the low-energy dynamics, which underlies the superconducting transition.

The peculiar changes in the optical properties of the cuprates at the onset of the superconducting phase[6–9] are particularly evident in pump and probe (p&p) experiments[12–17], where the pump-driven charge excitations modify the electron distribution resulting in a sudden destabilization of the condensate[18–20]. In such conditions, the *anomalous* connection, also observed at equilibrium, between the formation of the condensate and the high-energy optical transitions leads to the large changes in the time-resolved reflectivity (TRR) $R(\lambda, t)$ observed on the visible range[21–27].

Figure 1 shows our reflectivity data for 100 nm thick optimally doped YBCO films, grown by pulsed laser deposition on STO(001)[28], having a critical temperature $T_c=88$ K. The pump pulses are ≈ 80 fs long with central wavelength $\lambda_{pump} = 1300$ nm. The TRR was measured on a large spectral region with broadband white-light probes generated in a sapphire crystal ($400 \text{ nm} < \lambda_{probe} < 1000 \text{ nm}$; Energy $< 5 \mu\text{J}/\text{cm}^2$, see supplementary material for details and results). The transient reflectivity measurements, as reported in Fig.1a for $\lambda_{probe} = 560$ nm, manifestly show an oscillating component, which we associate to “coherent” phonon excitations. This oscillation, which is the main target of the present work, is superimposed to a decaying function of time, which we label as “incoherent”.

The coherent contribution is extracted by first fitting

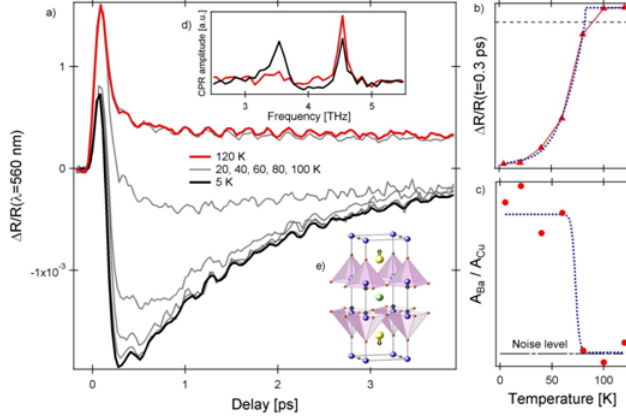


FIG. 1. (a) Transient reflectivity representative of the normal (red) and superconducting phase (black) at a probe wavelength of 560 nm (2.2 eV). (b) Relative variation of the incoherent reflectivity for a delay of 0.3 ps as a function of temperature and (c) ratio between the amplitudes of the Ba and Cu phonon modes vs. temperature. (d) Coherent contribution to the reflectivity as a function of frequency for $T=5$ K and 120 K. The peaks at 3.5 THz and 4.5 THz consist mainly of c-axis oscillations of the Ba and Cu positions, respectively (sketched in e).

$R(\lambda, t)$ for each λ with a multi-exponential decay convoluted with a step function, which provides the incoherent part, then a Fourier analysis of the difference between the data and the coherent part is performed. In Fig.1b we show the temperature evolution of the relative variation of the incoherent reflectivity $\Delta R/R$ for a 0.3 ps delay, while Fig. 1d reports the Fourier analysis of the oscillating part. The coherent response is indeed dramatically sensitive to the onset of superconductivity, as it consists of one single frequency (4.5 THz) above the critical temperature, while a second oscillation frequency (3.5 THz) appears below T_c (Fig.1d). The appearance of a second component below T_c is shown in Fig. 1c, where the ratio between the amplitude of the two modes is plotted. These frequencies correspond to two phonon modes observed in static Raman[29, 30] and time-resolved experiments[31–34], namely A_{1g} modes involving almost pure Ba and Cu off-plane vibrations respectively [30]. A displacive excitation of coherent phonon mechanism[35] has been invoked in order to describe the TRR in YBCO[36].

In order to rationalize the different behavior of the two low-frequency modes, we investigated the effect of coherent phonon distortions on the electronic structure by means of DFT calculations. We employed the generalized gradient approximation (PBE) using Quantum Espresso[37]. The experimental lattice parameters and ionic positions are taken from Ref. [38].

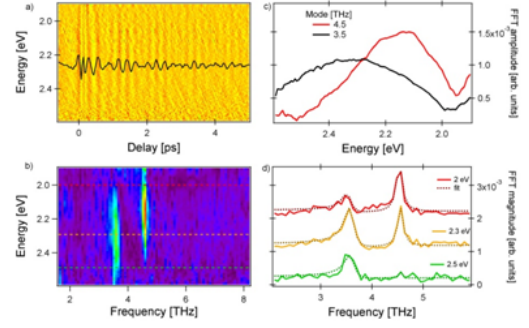


FIG. 2. (a) Amplitude of the coherent transient reflectivity (colours) at different wavelengths at 5 K and $20 \mu\text{J}/\text{cm}^2$ pump fluence (the black line is a representative cut at 560 nm). (b) Amplitude in the frequency-domain obtained by Fourier transforming the time traces. (c) Amplitude of the two relevant phonon modes at the different wavelengths, (d) line-shape representative of the different responses (dashed lines in b) with an offset added for clarity, and with the dotted lines obtained by a fit with Fano lineshape.

To highlight the effect of the coherent phonon excitation, we compare the electronic density of states calculated for YBCO at equilibrium with the ones obtained by artificially moving the Cu or Ba ions along the eigenvectors of the A_{1g} c-axis phonons of 0.116 \AA (1/100 of the unit cell). The calculation reveals that the density of states at the Fermi level is heavily modified by the Ba displacement while it is not considerably perturbed by the c-axis rearrangement of the Cu ions. The 4.52 states/eV value of the undistorted system becomes 3.26 and 4.82 for Ba and Cu displacement respectively. This result confirms that a perturbation of the low-energy electronic properties, such as the photo-induced quench of the superconducting gap is more coupled with a displacement of Ba atom, while the Cu displacement is essentially insensitive to the low-energy electrodynamics.

We now focus on the dependence on the probe wavelength (energy) of the coherent response in order to reveal the interplay between the displacement and the different electronic excitations. Fig.2a depicts, in a false color plot, the residual energy-dependent coherent contribution for the measurements at 5 K and $20 \mu\text{J}/\text{cm}^2$ of pump fluence. In Fig.2b, we plot the amplitude of the phonon modes at each photon energy. The Fourier transforms for representative energies are shown in Fig.2d. The wavelength-dependent coherent phonon response (CPR) amplitude for the two phonon modes plotted in Fig.2c are vertical cuts of Fig.2b taken at 4.5 THz for Cu and 3.5 THz for Ba. We have checked that these low-fluence CPR are in good agreement with the wavelength dependence of the Raman tensor[30].

In order to theoretically account for such a wavelength dependence, it is necessary to include the strong electron-electron correlations which are responsible for the insu-

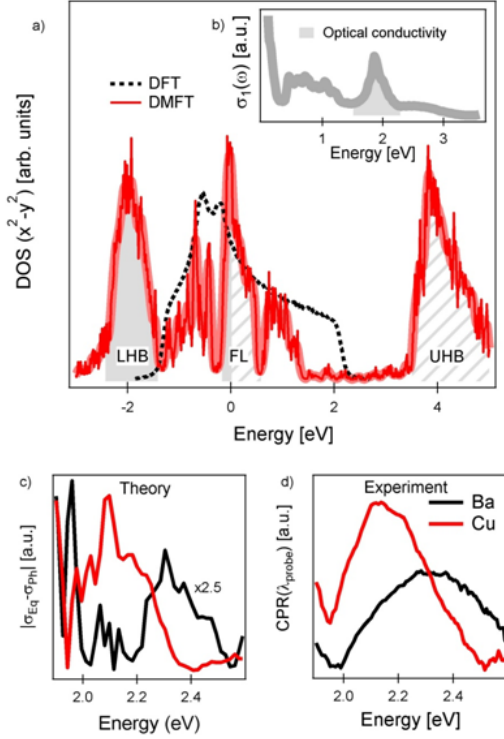


FIG. 3. (a) Density of states obtained in DMFT (red), compared with the DFT result (dashed black). (b) DMFT Optical conductivity (OC) (c) Calculated OC changes driven by the vibrational modes in the visible range (highlighted in grey in panel in (b)). The Ba response has been multiplied by 2.5, see text. (d) Energy-dependent amplitude of the coherent response measured in p&p experiments.

lating state of the parent compounds and of the optical spectral weight distribution[39]. This is implemented combining the DFT bandstructure with a DMFT treatment of the Coulomb interaction. We used a Wannier projection [40] including dx²-y² orbital and an on-site Coulomb repulsion on copper of $U = 4.8$ eV. We used exact diagonalization as the impurity solver with 8 sites in the bath.

In Fig.3a we compare the DMFT density of states with the uncorrelated results from DFT. The prime effect of the electronic correlation is to shift spectral weight to the lower Hubbard band (LHB) and an upper Hubbard band (UHB), which coexists with a low-energy structure corresponding to itinerant carriers with a renormalized bandwidth. In Fig.3b the real part of the optical conductivity $\sigma(\omega)$ calculated with DMFT is shown. As underlined by the gray shaded areas in Figs.3a and 3b, $\sigma(\omega)$ in the visible region is dominated by optical transitions between the LHB and the electronic states at the Fermi level. This observation enucleates the origin of the conductivity variations up to energies as high as few eV following the opening of a superconducting gap of the order of tens of meV.

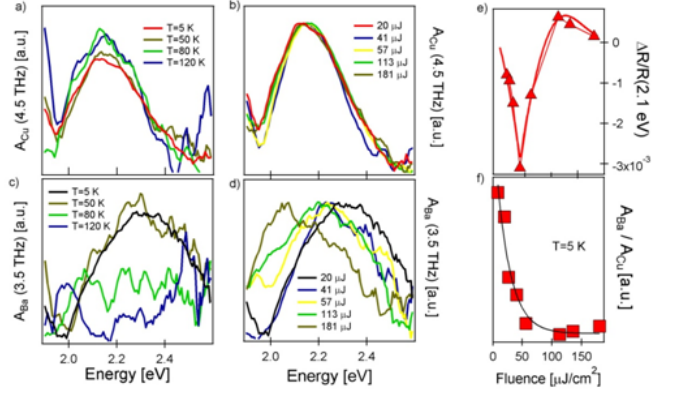


FIG. 4. (a-d) Amplitudes of the two vibrational modes as a function of wavelength for different temperatures (a,c) and excitation densities (b,d). (e) Amplitude of the incoherent part of $\Delta R/R$ and (f) ratio between the amplitudes of the coherent response of the two phonons. The amplitudes of the coherent phonon responses as a function of fluence have been renormalized in b and d to stress the wavelength dependence.

Here we rationalize the $\text{CPR}(\lambda_{\text{probe}})$ amplitude by means of a differential approach. We argue that the $\text{CPR}(\lambda_{\text{probe}})$ can be described qualitatively by the difference between $\sigma(\omega)$ calculated with the ions in the equilibrium position and that obtained with the ions displaced along the phonon eigenvector. Fig.3c displays the optical conductivity changes driven by the displacement of Cu (red) and Ba (black) ions along the c-axis. These differences are compared with the $\text{CPR}(\lambda_{\text{probe}})$ amplitude as a function of the probe energy for both phonon modes. Such a comparison shows that a proper treatment of the on-site Coulomb interaction on copper allows to correctly reproduce the dependence on the wavelength of the coherent response even in the single-site DMFT approximation without including other bands, longer-range interactions and explicit coupling to phonon modes. The quantitative mismatch in the amplitude could be due to the arbitrary absolute values for the distortion introduced in the calculation or, more interestingly, it could be ascribed to the anomalous Ba response, enhanced by superconductivity, which is not taken into account into the calculation, performed in the paramagnetic phase.

As we discussed above, the Cu mode is unaffected if we increase the base temperature of the sample. On the contrary the Ba mode disappears suddenly at $T > T_C$ (Fig.1c). In Fig.4a and 4c), we show that this behavior extends to the full wavelength-dependent $\text{CPR}(\lambda_{\text{probe}})$. The data for low pump fluence confirm that the Cu mode (Fig.4a) is essentially unaffected by raising the temperature above T_C while the fingerprint of the Ba mode (Fig.4b) on the optical properties disappears in the whole energy range.

We can further strengthen the connection between the phonon coherent response and the electronic properties

by increasing the pump fluence in our p&p measurements, reaching high-intensity perturbations, where the photo-excitation results in a partial or complete collapse of the superconducting gap[41, 42]. In Fig. 4e we show the effect of the increased fluence on the relative variation of the reflectivity $\Delta R/R$ at $\lambda_{probe} = 560$ nm after 0.3 ps delay (Fig. 4b) and 5 K. At low fluence this quantity is negative and increases in absolute value as the fluence grows. At the critical value $\Phi_C \approx 50 \mu\text{J}/\text{cm}^2$ a sharp kink is observed, followed by an increase of $\Delta R/R$ which eventually turns positive for fluences larger than $100 \mu\text{J}/\text{cm}^2$. This trend is a well-known signature of the photo-induced collapse of the superconducting gap observed in various compounds of the cuprate family[41–43].

Once again, the light-driven collapse of the superconducting phase is mirrored in the amplitude of the CPR(λ_{probe}) for the Ba and Cu modes. Figure 4f depicts the ratio between the amplitudes of the two modes as a function of fluence. Even if the behavior is less sharp than the temperature dependence of Fig.1c, the melting of the superconducting state is associated with the disappearance of the Ba peak. The wavelength-dependent CPR(λ_{probe}) are shown in Figs. 4b and 4d. The insensitivity of the Cu mode is confirmed, while the Ba mode is influenced also by the non-adiabatic melting of the superconducting gap (Fig.4c and Fig.4a, bottom right).

However, the effect of an increased pump fluence on the Ba mode does not mirror the effect of temperature. While the temperature essentially washes out the Ba phonon mode, an increased intensity rather leads to a change in the energy dependence of the CPR, even if the overall weight is reduced. This is suggestive of a non-thermal character of the pump-driven excitations, in agreement with recent time-domain photoemission experiments indicating that the pump pulse gives rise to excitations mainly in the antinodal regions[44, 45]. On the other hand a thermal excitation results in a large increase of excitations around the nodal points, where low-energy states are available, while no significant population changes are observed at the antinode[46]. Taking into account that the apical oxygens in YBCO are excited in p&p experiment within 150 fs, i.e. faster than the quasiparticles thermalization time[47], we can interpret our findings in terms of an effective momentum-dependent light driven dynamics of the superconducting gap. Further theoretical studies in the superconducting state including out-of-plane degrees of freedom are needed to substantiate this interesting scenario.

In summary, we addressed the interaction mechanism between the low-energy off-plane vibrations and the high-energy electronic in-plane excitations in superconducting cuprates by means of time-resolved ultra-fast reflectivity measurements, density functional theory, and dynamical mean field theory. The broadband optical probe allowed for the full dynamical characterization of the Raman tensor, confirming the existence of a c-axis barium vibration

that is strictly related to superconductivity in the copper-oxygen planes. With the aid of DFT and DMFT calculations we could identify the microscopical link between the off-plane modes and the electronic density of states.

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* daniele.fausti@elettra.eu

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